Energy transfer from phosphorescent blue-emitting oxidized porous silicon to rhodamine 110

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(Received 27 May 2010; accepted 17 October 2010; published online 29 October 2010)

Nanocomposites consisting of oxidized porous Si (OPSi) impregnated with rhodamine 110 (Rh110) molecules are characterized in terms of luminescence properties. The photoluminescence and its polarization memory strongly indicates a trace of energy transfer from the fast blue luminescence band of OPSi to the green one of Rh110. Time-resolved experiments showed that energy transfer to Rh110 also takes place from the long-lived blue phosphorescence of OPSi. The transfer channel from nonradiative states of OPSi to Rh110 was also found. The ability of OPSi to harvest and transfer absorbed photon energy to a guest is promising for applications in optoelectronics and biology. © *2010 American Institute of Physics*. [doi:10.1063/1.3511740]

Nanocrystalline porous silicon (PSi) can readily emit red-orange light as a result of quantum confinement effects.[1] The lifetime of this emission band is typically in the microsecond range, decreasing as the emission energy increases.[2] This emission has been made very efficient (external quantum efficiency up to 23%) and very stable by employing high-pressure water vapor annealing which provides outstanding surface passivation with stable and relaxed high-quality thin oxide.[3,4] The electroluminescence of PSi was also stabilized by high-pressure water vapor annealing.[5]

More recently, efficient blue photoluminescence (PL) (Ref. 6) and long-lived blue phosphorescence[7] have been reported in oxidized PSi (OPSi). The latter emission band was very much enhanced by high-pressure water vapor annealing. It can be observed for several seconds at low temperature and up to about 200 K after cutoff of the excitation. Contrary to the red band, the blue emission originates from molecularlike energy levels in OPSi, with the involvement of triplet states. The long lifetime of several seconds of the blue emission is potentially useful for photon harvesting and transferring energy to other species. In PSi layers impregnated with rhodamine B, rhodamine 6G, or both, energy transfer from red-emitting Si nanocrystals to the laser dyes has been evidenced by the analysis of the PL and its polarization memory (PM).[8–10]

Energy transfer from blue-emitting OPSi could find many applications, for example in lasing, sensing, and biofunctional substrates. In order to investigate the possibility of such energy transfer, rhodamine 110 (Rh110) has been chosen as the acceptor since its absorption band peaks at about 500 nm,[11] and thus overlaps partly with the blue emission band of OPSi (peaks at about 450 nm and extends up to 550 nm when excited at 266 nm).[7] In this paper, we present evidences of energy transfer from both the blue emission band and nonradiative defect states of OPSi to green-emitting Rh110 that was incorporated inside OPSi pores.

PSi and OPSi layers were prepared as previously reported,[7] from (100)-oriented and B-doped p-type (4 Ω cm) silicon wafers. PSi layers were 10 μm thick, exhibited a porosity of 68% and were only weakly luminescent in the conventional red band. OPSi consisted of a blue-emitting Si-rich porous oxide. Rh110 was introduced inside OPSi and PSi by impregnation for 10 min in an ethanoic solution of Rh110 (0.1 mM). Rh110 molecules are assumed to be attached uniformly onto the nanocrystalline silicon surfaces.

PL measurements were conducted either in air at room temperature or under vacuum in a cryostat for low temperature experiments. For luminescence excitation, a yttrium aluminum garnet (YAG) laser (266 nm; pulses of 12 ps; 10 Hz), an Ar laser (457.9; 488; and 514.5 nm) and a laser diode (410 nm) were used. The excitation intensity for the YAG laser was 2 mW/cm^2, and those for the Ar and diode lasers were about 0.3 W/cm^2. Cutoff filters with cutoff wavelengths of 540 nm, 500 nm, and 440 nm were used for excitation at 514.5 nm, 457.9 nm, and 410 nm, respectively. PL and PM spectra were measured using a fiber-optic spectrometer (Ocean Optics USB 2000). Time-resolved spectra were measured using a fiber-optic spectrometer (Hamamatsu C10029) coupled to a delay generator. The PM degree was determined by $PM=(I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp})$, where $I_{\parallel}$ and $I_{\perp}$ were the emission components polarized parallel and perpendicular to the polarization direction of the excitation light, respectively.[12]

Figure 1 shows the PL spectra of OPSi, PSi impregnated with Rh110, and OPSi impregnated with Rh110 for different excitation energies. At these excitation energies, the PL of OPSi is very weak as observed in Fig. 1(a), though the energy of 3.02 eV is sufficient to excite significantly the low energy tail of the blue emission band.

The PSi/Rh 110 composite is ideal for the study of Rh110 itself since the emission of PSi is very weak. A two-peak PL spectrum was observed at each excitation energy, as shown in Fig. 1(b). The red band peaked at about 1.6 eV can be attributed to the emission of nanocrystals in PSi. The

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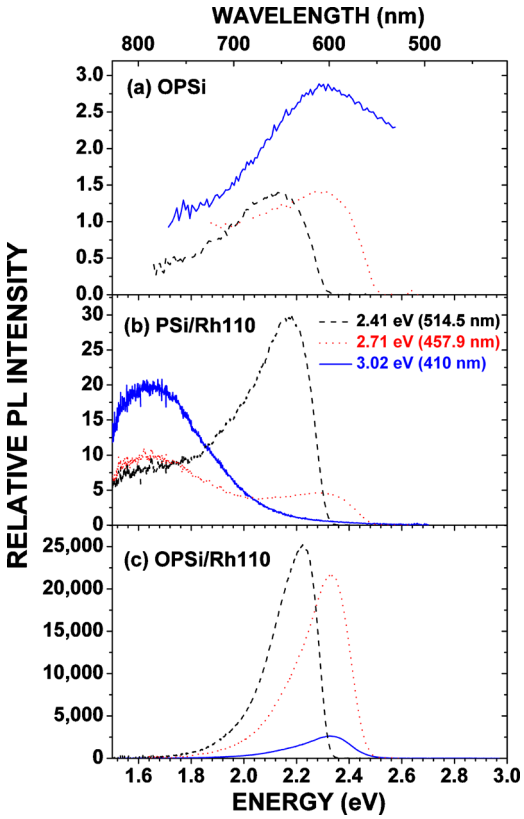

FIG. 1. (Color online) PL spectra of OPSi (a), PSi/Rh110 (b), and OPSi/Rh110 (c) layers under different excitation energies, at room temperature.

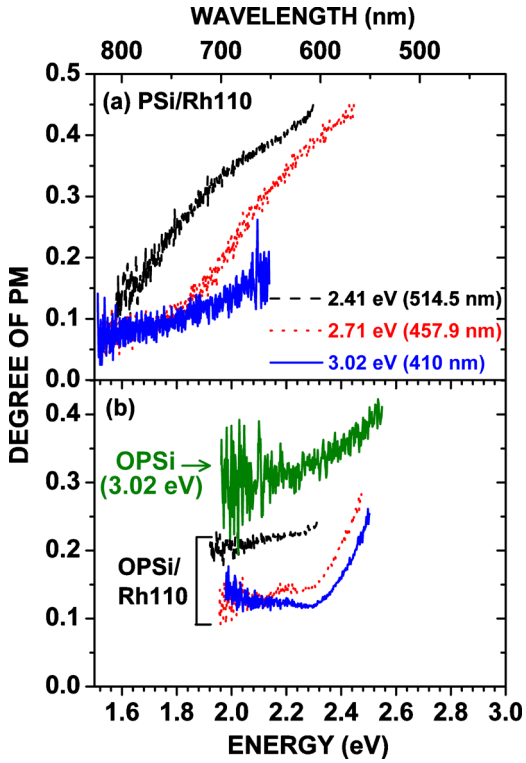

FIG. 2. (Color online) PM degree of PSi/Rh110 (a) and OPSi/Rh110 (b) layers under different excitation energies, at room temperature. The PM degree of OPSi under excitation energy 3.02 eV is also represented (b).

green band is the emission of Rh110. It is particularly strong when excited at 2.41 eV, because this energy is close to the peak of the absorption band of Rh110. At the excitation energy of 3.02 eV, the green emission of Rh110 cannot be directly excited since the absorption of Rh110 is very low at this energy. Thus, no emission of Rh 110 can be observed in this case.

In OPSi/Rh110, shown in Fig. 1(c), the green emission band is clearly observed for all the excitation energies, including 3.02 eV, which cannot excite Rh110 directly. Consequently, this result strongly suggests a form of energy transfer from OPSi to Rh110. We find in addition that the emission intensities of Rh110 are much higher than those observed in PSi/Rh110 [Fig. 1(b)]. This is consistent with the presence of significant energy transfer in OPSi/Rh110, although other possibilities (difference in the amount of adsorbed dye molecules[13] and absorption of excitation light by PSi) cannot be ruled out.

For the excitation energy 3.02 eV, the intensity of the blue band of OPSi [Fig. 1(a)] is much weaker than that of the green band of OPSi/Rh110 [Fig. 1(c)]. Therefore, the blue emission of OPSi cannot be the only excitation source of Rh110. This suggests that energy transfer from nonradiative states in OPSi to Rh110 also takes place.

In order to investigate the energy transfer from the blue band of OPSi to Rh110, PM experiments were conducted and the results are shown in Fig. 2. The PM degree of the green band of Rh110 is very high under direct excitation [Fig. 2(a)]. In fact, for energies close to the excitation, it is very close to the maximum value (0.5) possible for a random system of individual dipole emitters.[12] The PM degree of the blue emission band of OPSi is also large, as seen in Fig. 2(b). In the green emission band of OPSi/Rh110, however, the PM degree is much lower. Such a loss of PM is expected to take place during energy transfer processes.[10]

In order to investigate the contribution of the long-lived phosphorescence band on the energy transfer, time-resolved experiments were conducted on OPSi and OPSi/Rh110 samples at 5 K. In order to be able to compare these two samples with good confidence, they had to differ only by the presence of Rh110 in the pores. Thus, an OPSi sample was cut in half and only one half was impregnated with Rh110. In addition, all the experiments below were conducted exactly in the same conditions at the same time.

Figure 3 shows the luminescence spectra of OPSi and OPSi/Rh110 recorded with a gate time of 100 μs which included the laser pulse (12 ps). These samples exhibit a fast UV band (280–380 nm) as well as a fast blue band (380–470 nm) and a slow blue band (400–600 nm).[7] In Fig. 3, the intensity of the slow blue band is very weak compared to that of the UV band because the UV band is very fast (nanoseconds range or less), whereas the slow blue band is so slow that most excitons have not recombined yet within 100 μs after the laser pulse. Only OPSi/Rh110 exhibits a strong green band associated with Rh110. The emission peak of this green band is slightly blueshifted from that of Rh110 in ethanol, because of different environments of the molecules.[14]

Comparing the two samples, it is noticeable that both the UV band and the blue band around 490 nm are weaker in OPSi/Rh110 than in OPSi. These phenomena may be attributed partly to energy transfer toward Rh110, particularly for the blue band since it overlaps the absorption band of Rh110. Other possible origins for the reduced emission intensities include the absorption of excitation light by Rh110 and enhanced scattering behavior of the OPSi/Rh110 sample.

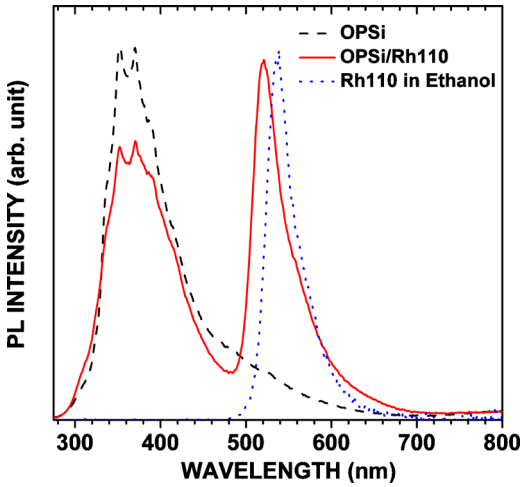

FIG. 3. (Color online) Luminescence spectra at 5 K of OPSi and OPSi/Rh110 under excitation at 266 nm. The gate time was 100 μs and included the laser pulse which lasted 12 ps. The normalized PL of Rh110 in ethanol, acquired at 300 K under excitation at 266 nm, is also represented.

In Fig. 4, we show the next spectra recorded after those shown in Fig. 3, i.e., with a gate and delay time of 100 μs. This gate time did not include the laser pulse. In OPSi, only the slow blue band can be observed, as expected.[7] In OPSi/Rh110, a green band characteristic of Rh110 emission was also observed. This emission of Rh110 was not expected, since its decay in PSi/Rh110 was very fast (ns range or less) at this temperature when directly excited at 488 nm. Its persistence for more than 100 μs suggests excitation via energy transfer. Furthermore, a clear dip in the spectrum of OPSi/Rh110 can be seen in the 460–500 nm range compared to that of OPSi. Since this energy range matches that of the absorption of Rh110, this phenomenon strongly suggests energy transfer from the slow blue band of OPSi to Rh110.

Figure 5 shows the normalized luminescence decay at 488 nm, which is within the dip discussed above, for both samples, and at 520 nm (representing the Rh110 emission) for OPSi/Rh110. In OPSi/Rh110, the decay of Rh110 at 520 nm is as slow as that of the blue band at 488 nm, and is

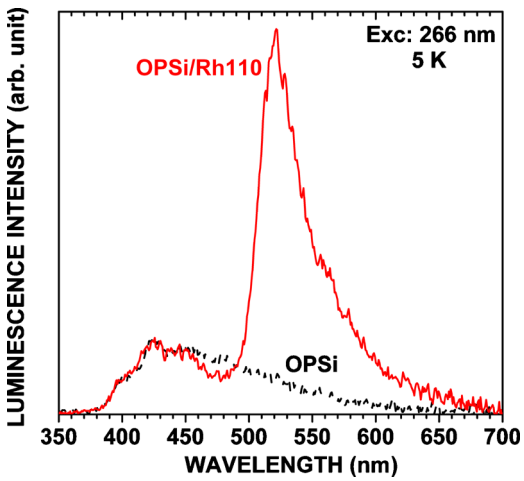

FIG. 4. (Color online) Luminescence spectra at 5 K of OPSi and OPSi/Rh110 under excitation at 266 nm, recorded 100 μs after the laser pulse of 12 ps. The gate time was 100 μs.

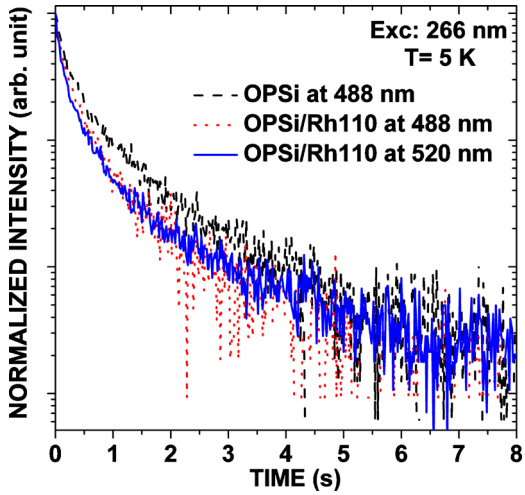

FIG. 5. (Color online) Normalized luminescence decay at 488 nm for OPSi and OPSi/Rh110, and at 520 nm for OPSi/Rh110, after the excitation at 266 nm was stopped. Gate and delay time was 20 ms.

slightly faster than that of OPSi luminescence at 488 nm. These results support the above conclusion that energy transfer takes place from the slow blue band to Rh110. The luminescence decay at 425 nm, at which the absorption by Rh110 is negligible, was not affected at all by the presence of Rh110 in the layers.

To conclude, energy transfer from both the fast blue emission band of OPSi and nonradiative defects in OPSi to Rh110 was verified by the analysis of PL and its PM. Energy transfer from the slow blue band of OPSi to Rh110 was also demonstrated by time-resolved luminescence measurements. The ability of OPSi to transfer its excitation toward other guest species may provide opportunities in various fields such as lasing, sensing and functional substrates for biology.

This work has been partially supported by Grants-in-Aid for Scientific Research on Priority Area (Grant No. 18063007) from MEXT-Japan, for Scientific Research A (Grant No. 18206039), and C (Grant No. 20560318) from JSPS.

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